

## **AQUA Progress report:**

### ***Infrared Laboratory Spectroscopy for AIRS, TES and HIRDLS***

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### **Proposal Summary**

The research objectives of this project are to support three **EOS** experiments (**AIRS**, **TES** and **HIRDLS**) by improving the database of air-broadened line shape parameters for water, nitrogen dioxide, methane and carbon monoxide in the 5 to 10  $\mu\text{m}$  spectral region. For the first two species, new laboratory measurements were obtained while for the last two, new measurements from other studies were evaluated and written into electronic format for immediate use by the instrument science teams and for future improvements to the **HITRAN** database.

### **Overview of Activities and Accomplishments**

To upgrade the line parameters, laboratory absorption spectra of air-broadened water and nitrogen dioxide at 6  $\mu\text{m}$  were measured and analyzed. These were recorded at high resolution with Fourier transform spectrometers at the National Solar Observatory (AZ) and the Pacific National Laboratory (WA). Retrieval and modeling software programs at William and Mary and JPL were revised in order to measure and analyze these data. For the 2004 HITRAN database, new air-broadened line shape parameters were collected for water, methane and carbon monoxide for the spectral regions used by AIRS, TES and HIRDLS. The temperature dependence coefficients determined from hot and cold water spectra were added to the database, along with other intensity and self-broadened results (obtained by Toth from other ongoing projects).

Review papers for a special issue of Journal of Quantitative Spectroscopy and Radiative Transfer were published to describe the available parameters and future needs for methane and other species.

In March, 2004, a manuscript was submitted to the Journal of Molecular Spectroscopy for the special Hougen issue describing new laboratory results of room and cold temperature air-broadened nitrogen dioxide; these will also be presented in June 2004 at the 59<sup>th</sup> Symposium for Molecular Spectroscopy in Columbus, OH.

### **Publications**

J.-M Flaud, C. Piccolo, B. Carli, A. Perrin, L. H. Coudert, J.-L. Teffo and L. R. Brown, Molecular line parameters for the **MIPAS** (Michelson Interferometer for Passive Atmospheric Sounding) experiment, *Atmospheric and Oceanic Optics* 16, 172-182, 2003.

L. R. Brown, D. Chris Benner, J.P. Champion, V.M. Devi, L. Fejard, R.R. Gamache, T. Gabard, J.C. Hilico, B. Lavorel, M. Loete, G. Ch. Mellau, A. Nikitin, A. S. Pine, A. Predoi-Cross, C. P. Rinsland, O. Robert, R. L. Sams, M.A.H. Smith, S. A. Tashkun, and Vl. G. Tyuterev, Methane line parameters in HITRAN, *J. Quant. Spectrosc. Rad. Transfer.* 82, 219-238 (2003).

L.S. Rothman, A. Barbe, D.C. Benner, L.R. Brown, C. Camy-Peyret, M.R. Carleer, K. Chance, C. Clerbaux, V. Dana, V.M. Devi, A. Fayt, J.-M. Flaud, R.R. Gamache, A. Goldman, D. Jacquemart, K.W. Jucks, W.J.Lafferty, J.-Y. Mandin, S.T. Massie, V.Nemtchinov, D.A. Newnham, A. Perrin, C.P. Rinsland, J. Schroeder, K.M. Smith, M.A.H. Smith, K. Tang, R.A. Toth, J. Vander Auwera, P. Varanasi and K. Yoshino, The HITRAN Molecular Spectroscopic Database: Edition of 2000 Including Updates through 2001, to *J. Quant. Spectrosc. Rad. Transfer.* **82**, 5-44 (2003).

D. Chris Benner, T. A. Blake, L. R. Brown, V. Malathy Devi, M.A.H. Smith and R. A. Toth, Air-broadening parameters in the v<sub>3</sub> band of <sup>14</sup>N<sup>16</sup>O<sub>2</sub> using a multispectrum fitting technique (submitted to *J. Mol. Spectrosc.*)

R. A. Toth, L. R. Brown, M. A. H. Smith, V. Malathy Devi, D. Chris Benner and M. Dulick, Temperature dependence of air-broadened line widths and shifts of H<sub>2</sub>O at 6  $\mu$ m, (to be submitted).

### **Plans for the remainder of the task**

In 2004, some retrievals of air-broadened water will be done at 2.7  $\mu$ m to test the accuracy of our temperature dependence coefficients. These will be validated by Geoff Toon and Bhaswar Sen at JPL by comparison of observed and synthetic atmospheric ground-based spectra. Finally, manuscripts will be prepared to document our water results in the open literature. The individual measurements will be deposited with the journal to be used for future studies, such as the theoretical modeling of line shape parameters. The values will be transmitted to R. Gamache who is performing quantum mechanical modeling of widths and shifts.

### **Archival strategy**

The resulting databases for water, nitrogen dioxide, methane, and carbon dioxide were transmitted electronically to the science teams for TES which is being given to the HIRDLS team..

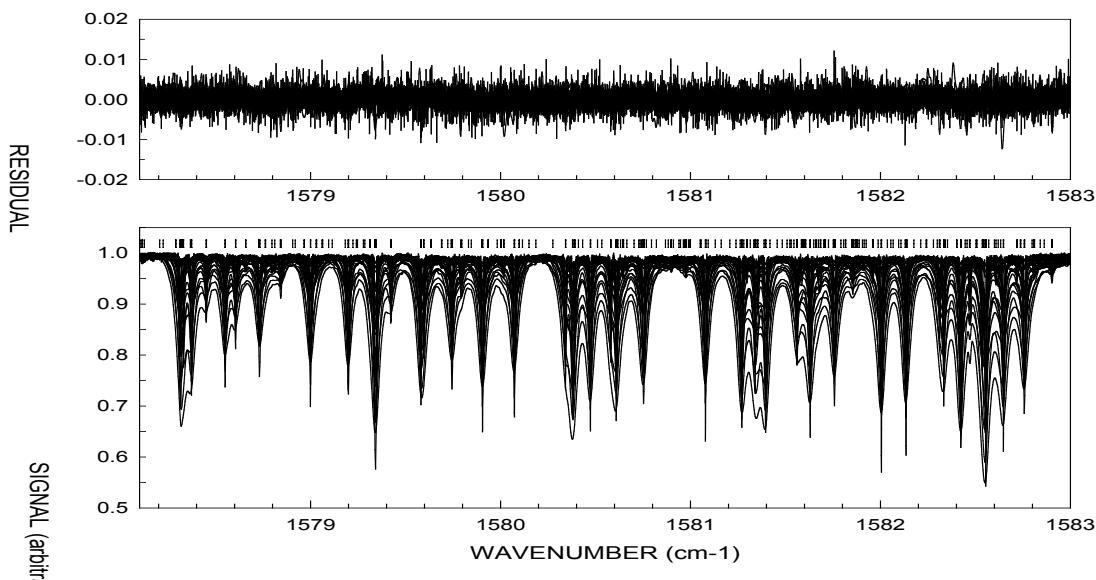
The databases are submitted for inclusion in HITRAN and GEISA.

Manuscripts describing the databases will be submitted to peer-reviewed journals (such as *J. Quant. Spectrosc. Rad. Transfer*).

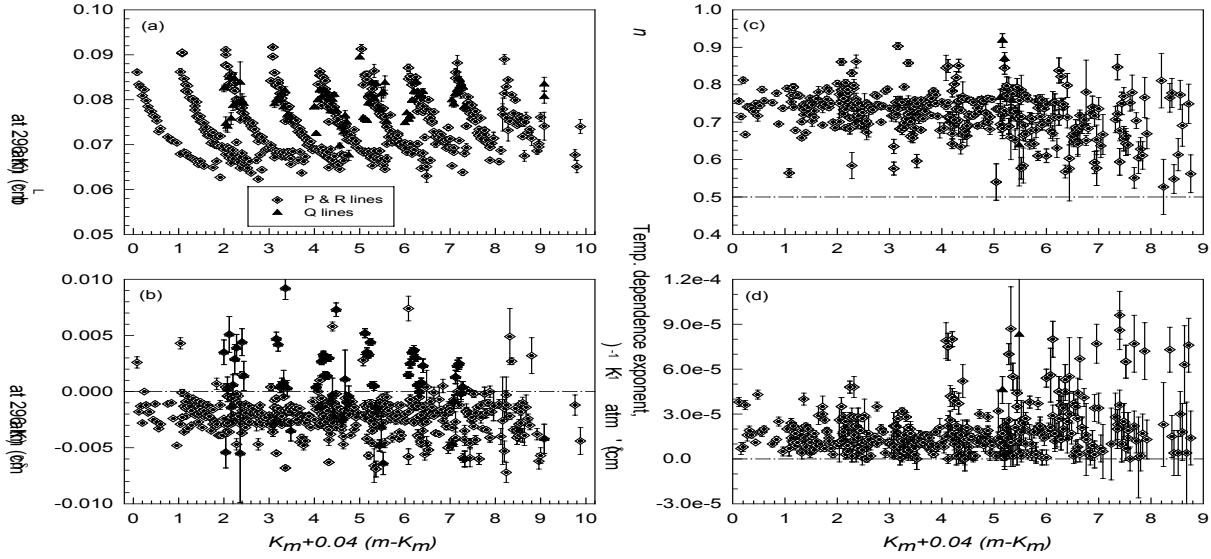
## *NO<sub>2</sub>: air-broadened line widths and shifts at room and cold temperatures.*

Air-broadened line widths, pressure-induced shift coefficients and their temperature dependences were retrieved for over 1000 transitions in the v<sub>3</sub> band of <sup>14</sup>N<sup>16</sup>O<sub>2</sub> at 6 m. In addition, precise line center positions and relative intensities were also determined. The results were obtained by fitting simultaneously 27 spectra recorded at high resolution (0.002 cm<sup>-1</sup> to 0.006 cm<sup>-1</sup>) with two Fourier transform spectrometers and gas sample temperatures ranging from 206 K to 298 K. In Fig. 1, a sample retrieval is shown. For this, it was necessary to modify the multispectrum fitting software to accommodate constraints on the retrieved parameters of closely-spaced spin-split doublets in order to successfully determine their broadening and shift parameters. One component of adjacent transitions with the same rotational quantum numbers was allowed to adjust while the other spin component was constrained to have broadening coefficients equal to the free component. Where necessary, intensity ratios of the spin split components were constrained using the calculated intensities in the database.

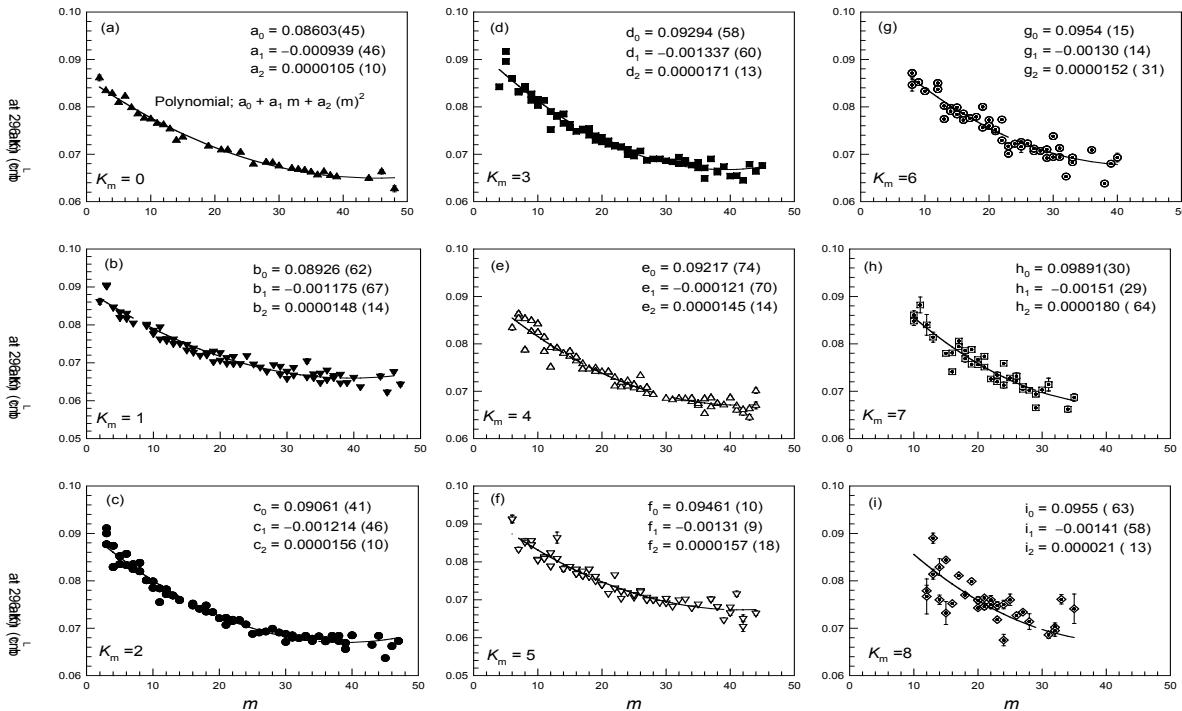
The variations of the widths, shifts and their temperature dependences with the quantum numbers were investigated. Figure 2 has plots of all the measured broadening coefficients as a function of the quantum numbers. Subsets of the observed line widths were reproduced to within 3% using empirical smoothing functions, as seen in Fig. 3. Some of the pressure shifts could be calculated in a similar fashion, as seen in Fig. 4. These empirical models provide the mechanism to update the line shape parameters on the HITRAN database.



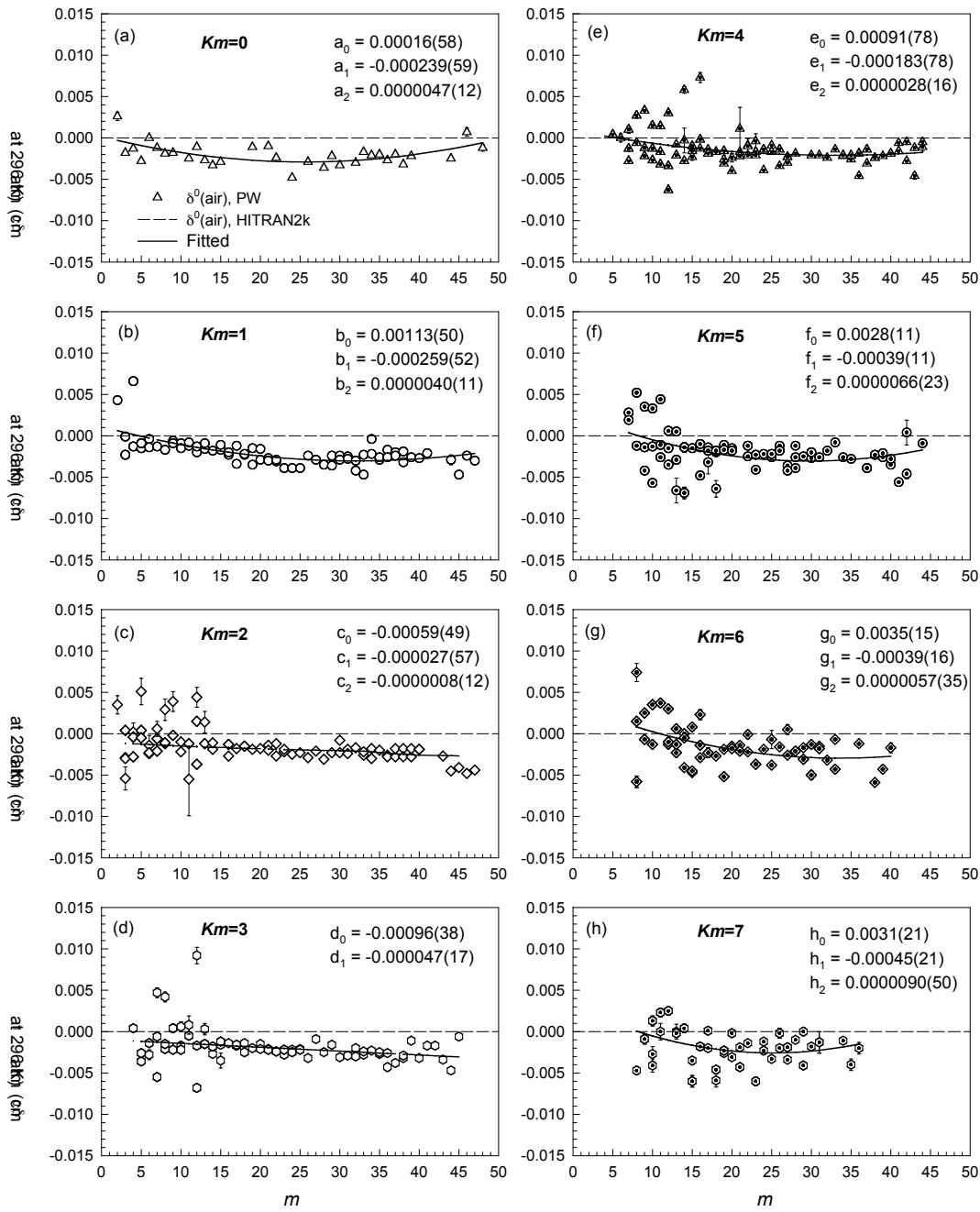
**Fig. 1. A multispectrum fit region near 1580 cm<sup>-1</sup>. The observed spectra are plotted in the lower panel (b), and the magnified residuals (observed minus calculated) obtained from the least squares fit are shown in the upper panel (a). There are 27 spectra included in this fit.**



**Fig. 2** Measured air-broadening coefficients plotted as a function of  $K_m+0.04$  ( $m-K_m$ ). The value of  $m$  is the lower state  $N$  for P and Q branch lines and the upper state  $N$  for R branch lines ;  $K_m$  is equal to  $K_a$ . (a)  $b_L^0(\text{air})$  in  $\text{cm}^{-1} \text{ atm}^{-1}$  at 296 K (b) Measured air-induced pressure shift coefficients,  $\delta^0(\text{air})$ , in units of  $\text{cm}^{-1} \text{ atm}^{-1}$  at 296 K. (c) the temperature dependence of the line widths (d) the temperature dependence of the pressure shifts. Where no error bars are visible the uncertainties in the measurements are smaller than the symbol size used.



**Fig. 3** Variation of  $b_L^0(\text{air})$  with  $m$  for (a)  $K_m=0$ , (b)  $K_m=1$ , (c)  $K_m=2$ , (d)  $K_m=3$ , (e)  $K_m=4$ , (f)  $K_m=5$ , (g)  $K_m=6$ , (h)  $K_m=7$  (g) and (i)  $K_m=8$ . Where error bars are not visible the uncertainties in the measured broadening coefficients are smaller than the size of the symbols used. In each panel the solid line denotes the fitted polynomial curve for each value of  $K_m$ . Also given in each panel are the coefficients of the polynomials resulting from the fits.



**Fig. 4 Variation of  $\delta^0(\text{air})$  with  $m$  for (a)  $Km=0$ , (b)  $Km=1$ , (c)  $Km=2$ , (d)  $Km=3$ , (e)  $Km=4$ , (f)  $Km=5$ , (g)  $Km=6$  and (h)  $Km=7$ . The value of  $m$  is lower state N for P and Q branch lines and upper state N for R branch lines. Where error bars are not visible the uncertainties in the measured broadening coefficients are smaller than the size of the symbols used. In each panel the solid line denotes the fitted polynomial curve of Eq. (8) for each value of  $Km$ . Also given in each panel are the polynomial coefficients best fit to the data**